



# A stable $\text{Ag}_3\text{PO}_4$ @PANI core@shell hybrid: Enrichment photocatalytic degradation with $\pi$ - $\pi$ conjugation



Li Liu, Lan Ding, Yongguang Liu, Weijia An, Shuanglong Lin, Yinghua Liang, Wenquan Cui\*

College of Chemical Engineering, Hebei Key Laboratory for Environment Photocatalytic and Electrocatalytic Materials, North China University of Science and Technology, Tangshan 063009, PR China

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## ABSTRACT

Here we report an  $\text{Ag}_3\text{PO}_4$ @PANI visible photocatalyst with core@shell structure prepared by a chemisorption method. The photocatalytic activity of  $\text{Ag}_3\text{PO}_4$ @PANI was enhanced significantly with increasing proportion of PANI. The high photocatalytic performance for the degradation of phenol and 2,4-dichlorophenol over  $\text{Ag}_3\text{PO}_4$ @PANI (5 wt.%) composite photocatalyst reached 100% and 95.3%, which were 1.44 and 1.38 times of that of bulk  $\text{Ag}_3\text{PO}_4$ , respectively. The photocatalytic activity of  $\text{Ag}_3\text{PO}_4$ @PANI remained 85% after five cycling runs, whereas the activities of M- $\text{Ag}_3\text{PO}_4$ /PANI (5 wt.%) and  $\text{Ag}_3\text{PO}_4$  remained 42% and 24%, respectively, indicating that  $\text{Ag}_3\text{PO}_4$ @PANI photocatalyst possessed a superior stability. Further analyses showed that the enhancement of photocatalytic activity and photo-stability originated from the superior charge mobility derived from the  $\pi$ -conjugated structure of PANI and the hybridization effect arising from  $\text{Ag}_3\text{PO}_4$  and PANI. Moreover, the matched energy level between PANI and  $\text{Ag}_3\text{PO}_4$  led to the efficient separation and transfer of photo-generated electron-hole at their interface, thus improving the photocatalytic performance of  $\text{Ag}_3\text{PO}_4$ @PANI composite. In addition, PANI shell can prevent the dissolution of  $\text{Ag}_3\text{PO}_4$  particles in aqueous solution during the photocatalytic reaction, resulting in a high stability of the  $\text{Ag}_3\text{PO}_4$ @PANI composite photocatalyst.

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## 1. Introduction

Photocatalysts, especially those with high photocatalytic activity and strong stability under visible light, have been regarded as promising materials for applications in solar energy conversion and treatment of water pollution [1,2]. Although  $\text{TiO}_2$  is the most investigated photocatalyst so far [3], the wide energy gap (3.2 eV) of  $\text{TiO}_2$  has hindered its sufficient utilization of sunlight [4,5]. Therefore, the development of novel and more efficient visible-light-driven (VLD) photocatalysts is still urgently needed from the viewpoint of solar energy utilization.

$\text{Ag}_3\text{PO}_4$  based photocatalysts have attracted considerable attention because of their excellent visible-light-driven photocatalytic activities for the degradation of organic pollutants and a broad band gap of 2.45 eV [6]. As a photocatalyst,  $\text{Ag}_3\text{PO}_4$  has an indirect band gap and photo-excited holes with strong oxidation capability in the VB, and the mobility of the electron is significantly higher than that

of the hole. This facilitates the separation of electron-hole pairs partially because of the formation of the delocalized  $\pi^*$  antibonding states in the CB. In addition, the inductive effect of  $\text{PO}_4^{3-}$  facilitates the  $e^-/h^+$  separation, which considerably contributes to its excellent photocatalytic activity [7]. Ye and co-workers [8] discovered that  $\text{Ag}_3\text{PO}_4$  possessed extremely high photo-oxidative capabilities for  $\text{O}_2$  evolution from water as well as for organic dye degradation under visible light irradiation with a quantum efficiency of 90% at wavelengths greater than 520 nm, which is dozens of times higher than those of traditional photocatalytic materials  $\text{TiO}_2\text{-xN}_x$ , thus illustrating that  $\text{Ag}_3\text{PO}_4$  has a tremendous potential for applications in photocatalytic materials. More interestingly, it has been recently revealed that uniform colloidal  $\text{Ag}_3\text{PO}_4$  nanocrystals with a precise control of particle size ranging from 8 to 16 nm showed higher catalytic activity in the photodecomposition of MB under visible light irradiation than traditional photocatalysts, such as N-doped  $\text{TiO}_2$ -P25 and  $\text{TiO}_2$ -P25 [9]. However, the practical application of  $\text{Ag}_3\text{PO}_4$  is severely limited by some drawbacks, including the severe photo-corrosion in photocatalysis process, which restricts the recycle and efficiency of the  $\text{Ag}_3\text{PO}_4$  composite photocatalysts [10,11]. In addition,  $\text{Ag}_3\text{PO}_4$  photocatalyst could slightly dissolve as  $\text{Ag}^+$

\* Corresponding author.

E-mail address: [wkui@163.com](mailto:wkui@163.com) (W. Cui).

and  $\text{PO}_4^{3-}$  in aqueous solution, thus reducing the photocatalytic activity and stability of  $\text{Ag}_3\text{PO}_4$ . These adverse effects could be alleviated by blend with  $\text{Fe}_2\text{O}_3$  [12],  $\text{AgI}$  [13] and  $\text{ZnO}$  [14] that could accelerate the photo-induced charge separation.

Photocatalysts with core@shell structures possess excellent visible-light-driven photocatalytic activity and many other advantages [15–17]. The stabilized material sheets coated on the surface of  $\text{Ag}_3\text{PO}_4$  particles can prevent the dissolution of  $\text{Ag}_3\text{PO}_4$  in aqueous solution, thus enhancing the structural stability of  $\text{Ag}_3\text{PO}_4$ -based core@shell photocatalysts during the photocatalytic reaction [18]. The large contact area between core and shell can facilitate the separation of the photo-generated charge carriers at their interface. In addition, the coupling of  $\text{Ag}_3\text{PO}_4$  with semiconductors can form a strong electric field at the interface near the band-edge offset, which can significantly accelerate the transfer of photo-generated charge carriers. Therefore, the shell materials that can facilitate the charge transfer and separation are strongly desired. To date,  $\text{Ag}_3\text{PO}_4$ -based core-shell materials, such as  $\text{BiPO}_4$  [19] and  $\text{AgBr}$  [20], generally exhibit point contact between the bulk phases, which lead to a weak conjunction of  $\text{Ag}_3\text{PO}_4$  with semiconductors and could significantly limit the photo-induced charge separation. Therefore, there is the need to continue to explore novel core-shell materials for improving the activity and stability of  $\text{Ag}_3\text{PO}_4$  photocatalyst.

Nowadays, delocalized  $\pi$ - $\pi$  conjugated structures have been proven to induce a rapid photo-induced charge separation and to decrease the charge recombination rate in electron-transfer processes [21–23]. Recently, many research teams have developed some hybrid semiconductors from delocalized conjugative  $\pi$  structure materials as efficient photocatalysts, such as graphene [24], carbon nitride [25], and conductive polyaniline (PANI) [26]. In these studies, the delocalized conjugated materials closely matched with the photocatalysts in energy level, and an intensive interface hybrid effect emerged between conjugated materials, resulting in rapid charge separation and slow charge recombination in the electron-transfer process. Previously, our group reported that conjugative  $\pi$  structure of g- $\text{C}_3\text{N}_4$  nano-sheets coated on the surface of  $\text{Ag}_3\text{PO}_4$  particles with core@shell structure can significantly enhance the photocatalytic activity and stability [27]. Polyaniline (PANI) is one of the conductive polymers having a delocalized  $\pi$ - $\pi$  conjugated structure, in which the benzenoid and quinonoid units have several redox states with many other interesting properties [28]. Moreover, PANI is a promising candidate for large-scale applications due to its high conductivity, superior environmental stability, and convenient preparation. The combination of PANI with semiconductor improved the migration efficiency of charge carriers at the interface between PANI and semiconductor because of the superior charge carrier mobility of PANI, thereby facilitating the separation of photo-generated charge carriers and enhancing the photoelectrocatalytic performance. Zhu et al. [29] reported that the hybridization with monolayer PANI not only enhanced the photocatalytic activity but also remarkably inhibited the photo-corrosion of  $\text{ZnO}$ . Similarly, Wang et al. [30] prepared PANI@CdS core-shell nano-spheres by a proton doped in-situ polymerization method and demonstrated that the PANI@CdS substantially enhanced photocatalytic hydrogen production and photo-corrosion inhibition.

Herein, we reported a novel stable  $\text{Ag}_3\text{PO}_4$ @PANI core@shell composite photocatalyst by a chemisorption method. Our result demonstrated the shell PANI could prevent the dissolution of  $\text{Ag}_3\text{PO}_4$  in aqueous solution, thus enhancing the structural stability of  $\text{Ag}_3\text{PO}_4$ . Meanwhile, the  $\pi$ - $\pi$  conjugation in the structure of PANI and a strong interaction in the intimate contact interface resulted in an ultrafast conductivity, which efficiently facilitated the migration of interfacial charge carriers and the separation of photo-generated electrons and holes. This synergistic effect led to the suppression

of photo-corrosion of  $\text{Ag}_3\text{PO}_4$  and generation of dramatic visible photocatalytic activity and photo-stability. The  $\text{Ag}_3\text{PO}_4$ @PANI (5 wt.%) composite exhibited higher visible light photocatalytic degradation activity and stability than bare  $\text{Ag}_3\text{PO}_4$  particles. The deep photo-oxidation activities for the degradation of phenol and 2,4-dichlorophenol over  $\text{Ag}_3\text{PO}_4$ @PANI (5 wt.%) composite photocatalyst reached 100% and 95.3%, which were respectively 1.4 and 1.7 times of that of bulk  $\text{Ag}_3\text{PO}_4$ .

## 2. Experimental

### 2.1. Synthesis of $\text{Ag}_3\text{PO}_4$

$\text{Ag}_3\text{PO}_4$  was prepared by a precipitation method. Briefly, 0.8 g PVP was suspended in 40 mL distilled water, followed by the addition of 0.8 g  $\text{AgNO}_3$ .  $\text{Na}_2\text{HPO}_4$  solution was prepared by dissolving 0.288 g  $\text{Na}_2\text{HPO}_4$  in 20 mL distilled water and added to the PVP- $\text{AgNO}_3$  aqueous solution dropwise under stirring. The mixed solution was stirred for 1 h and centrifuged. The precipitate was collected, washed with water and ethanol for three times and dried at 60 °C for 12 h.

### 2.2. Synthesis of core@shell $\text{Ag}_3\text{PO}_4$ @PANI

The  $\text{Ag}_3\text{PO}_4$ @PANI photocatalysts were fabricated as follows: a certain amount of  $\text{Ag}_3\text{PO}_4$  powder was added to 100 mL of 0.45 g/L PANI (THF) solution with sonication for 30 min, and then the mixture was stirred for 48 h. The nominal weight ratios of PANI to  $\text{Ag}_3\text{PO}_4$  were 1, 2, 5, 10, 15, and 20 wt.%, and the weights of  $\text{Ag}_3\text{PO}_4$  were 1.2 g, 0.24 g, 0.17 g, 0.13 g and 0.12 g, respectively. After evaporation of water, the resulting residue was dried at 60 °C for 24 h to afford an  $\text{Ag}_3\text{PO}_4$ @PANI composite powder. The sample named M- $\text{Ag}_3\text{PO}_4$ /PANI (5 wt.%) was prepared by the direct mechanical mixing of  $\text{Ag}_3\text{PO}_4$  and PANI (5 wt.%) in an agate mortar.

### 2.3. Characterization of photocatalysts

The crystal structures and phase states of  $\text{Ag}_3\text{PO}_4$ @PANI composites were determined by X-ray diffractometry (XRD) using a Rigaku D/MAX2500 PC diffractometer with Cu K $\alpha$  radiation at an operating voltage of 40 kV and an operating current of 100 mA. The morphologies of the samples were imaged with a scanning electron microscopy (SEM) (Hitachi, S-4800) and a transmission electron microscopy (TEM) (JEOL Ltd., JEM-2010). UV-vis (UV-vis) diffuse reflectance spectra were recorded on a UV-vis spectrometer (Puxi, UV1901). The band gap energies were calculated from a plot  $(\alpha h\nu)^{1/2}$  vs. photo-energy ( $h\nu$ ) using the Kubelka-Munk function which shows the relationship of band gap  $E_g$  and absorption coefficient  $\alpha$ . The equation is as follows:  $\alpha h\nu = A(h\nu - E_g)^{1/2}$ . Where  $\alpha$  is the absorption coefficient,  $\nu$  is the frequency of the light, and  $h$  is Planck's constant. The Fourier transform infrared spectra (FTIR) of the samples were recorded on an IR Vertex70 FTIR spectrometer. Raman spectra were recorded on a microscopic confocal Raman spectrometer (Thermo Electron DXR) with an excitation of 785 nm laser light. Chemical states of these photocatalysts were analyzed with X-ray photoelectron spectroscopy (XPS) on an XSAM800 apparatus. Electrochemical and photo electrochemical measurements were performed in 0.1 M  $\text{Na}_2\text{SO}_4$  electrolyte solution in a three-electrode quartz cell. Pt sheet was used as a counter electrode, and  $\text{Hg}/\text{Hg}_2\text{Cl}_2/\text{sat. KCl}$  was used as a reference electrode. The  $\text{Ag}_3\text{PO}_4$ @PANI composite thin film on an indium-tin oxide (ITO) was used as the working electrode for investigation. The photo electrochemical response was recorded with a CHI 660B electrochemical system. The  $\text{Ag}^+$  concentration in the solution was determined by Inductively Coupled Plasma (ICP) (HORIBA, ULTIMA2). To study the

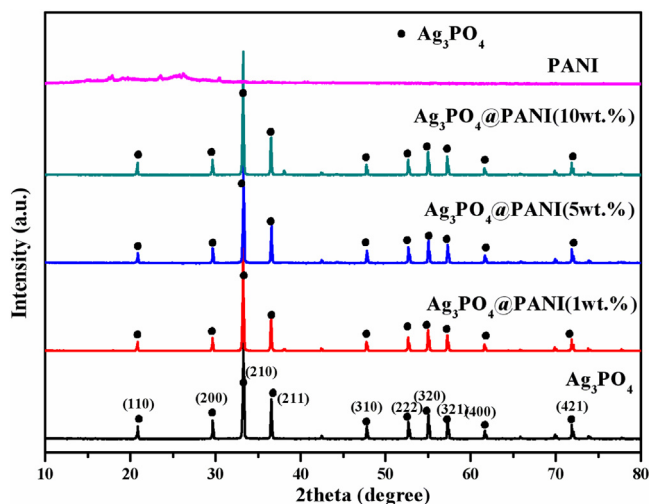


Fig. 1. XRD patterns of PANI,  $\text{Ag}_3\text{PO}_4$ , and  $\text{Ag}_3\text{PO}_4$ @PANI photocatalysts.

recombination of photo induced charge carrier, photoluminescence (PL, Hitachi F-7000, 250 nm) were measured.

#### 2.4. Photocatalytic activity

The photocatalytic activities of the as-prepared samples were evaluated by the degradation of phenol solution in a multi-tube agitated reactor (XPA-7). The photocatalytic activity of  $\text{Ag}_3\text{PO}_4$ @PANI composite was evaluated by catalytic degradation of phenol under visible light irradiation. A 250 W halide lamp (Royal Philips, Amsterdam, The Netherlands, flux is 17500 lm) with a 420 nm cutoff filter was used at a distance of 10 cm from an unsealed beaker. A glass reactor with  $25 \pm 2^\circ\text{C}$  external circulating water was employed for the test group. 0.05 g photocatalyst was added to 50 mL of 10 mg/L phenol solution. Before the light irradiation, the suspensions were magnetically stirred for 30 min to reach the adsorption-desorption equilibrium. At given time interval, 3 mL aliquots were sampled and filtered with a micro-pore membrane. Simultaneously, the filtrates of phenol solutions at different conditions were analyzed by recording variations of the phenol peak area. HPLC was adopted for analysis of phenol concentration and the distribution of its degradation products. The mobile phase was composed of methanol and water (volume ratio: 60/40), and the elution time was 6 min at a flow rate of 1 mL/min. The detector was set at the wavelength of 270 nm, and C18 reversed phase column (Agilent 1100, 4.6 nm  $\times$  200 nm) was used for chromatographic analysis. The conditions for the degradation of 2, 4-dichlorophenol were similar to those of phenol under visible light irradiation.

### 3. Results and discussion

The XRD measurements were carried out to determine the crystalline structure of PANI,  $\text{Ag}_3\text{PO}_4$ , and  $\text{Ag}_3\text{PO}_4$ @PANI composites (Fig. 1). In the case of the bare  $\text{Ag}_3\text{PO}_4$ , all of the diffraction peaks could be clearly indexed to the cubic phase of  $\text{Ag}_3\text{PO}_4$  (JCPDS card No. 06-0505). This phase could be characterized by the appearance of Bragg diffraction peaks at  $2\theta = 20.9^\circ$ ,  $29.7^\circ$ ,  $33.3^\circ$ ,  $36.6^\circ$ ,  $47.8^\circ$ ,  $52.7^\circ$ ,  $55.0^\circ$ ,  $57.3^\circ$ ,  $61.6^\circ$  and  $71.9^\circ$ , which were indexed to (110), (200), (210), (211), (310), (222), (320), (321), (400) and (421) planes for  $\text{Ag}_3\text{PO}_4$ , respectively. Compared with bare  $\text{Ag}_3\text{PO}_4$ , the XRD patterns of core@shell structure  $\text{Ag}_3\text{PO}_4$ @PANI did not vary in peaks or shapes. This finding indicated that coating on the PANI shell did not effect on the crystal structure of  $\text{Ag}_3\text{PO}_4$ . Moreover, no characteristic diffraction peaks of PANI were detected in  $\text{Ag}_3\text{PO}_4$ @PANI

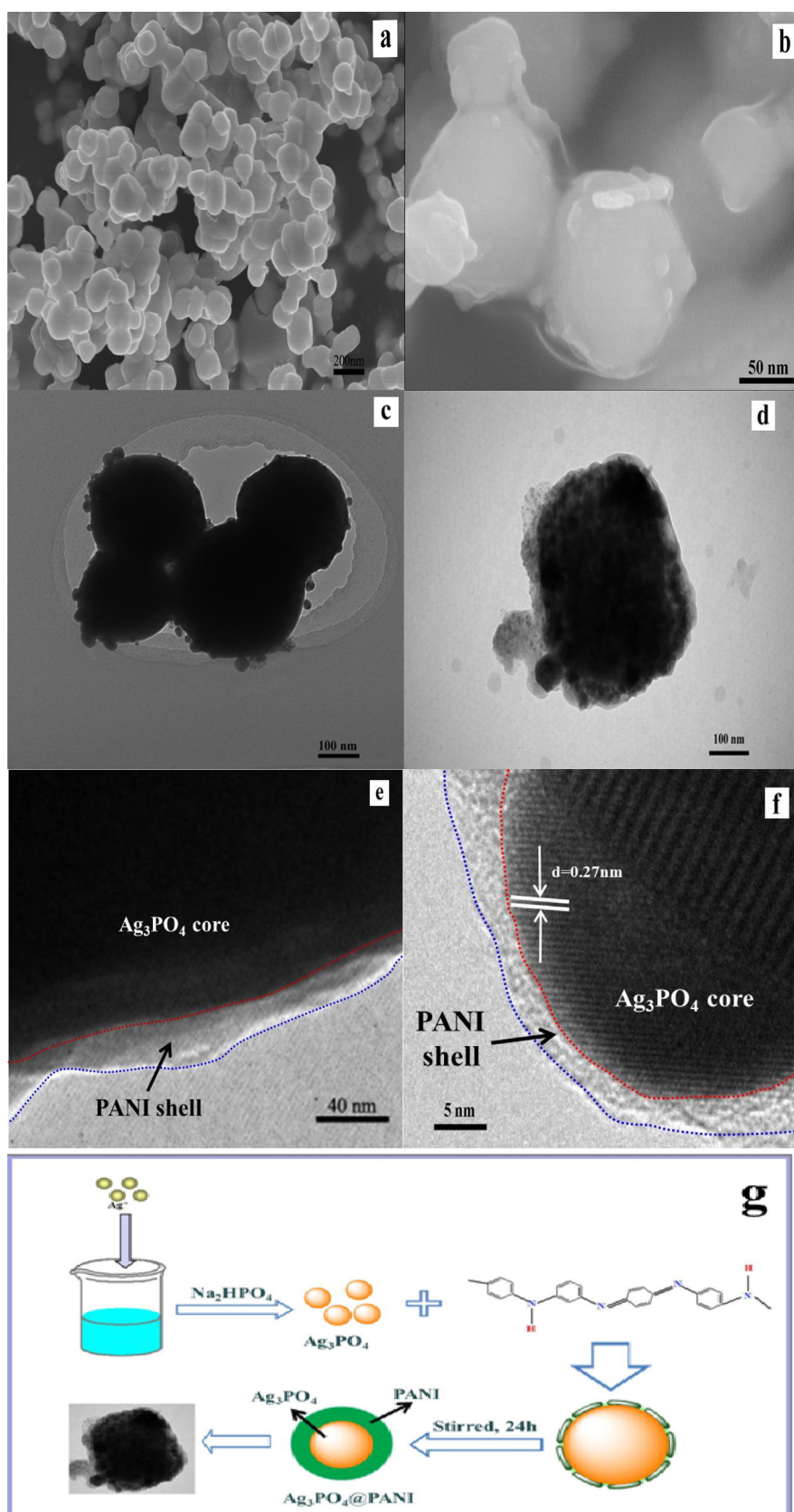
composite because PANI is amorphous in the composite photocatalyst [31].

The morphologies and microstructures of the as-prepared samples were studied by SEM and TEM, as shown in Fig. 2. Fig. 2a shows the SEM image of the pure  $\text{Ag}_3\text{PO}_4$ . It could be seen that the  $\text{Ag}_3\text{PO}_4$  particles were uniform in size with the estimated average diameter ranging from 200 to 300 nm. Fig. 2b is the high-magnification SEM image of the  $\text{Ag}_3\text{PO}_4$ @PANI core@shell composite. It can be seen clearly that the PANI shell was uniformly coated on the surface of  $\text{Ag}_3\text{PO}_4$  particles. Fig. 2c shows the TEM image of the pure  $\text{Ag}_3\text{PO}_4$ . In Fig. 2c, the estimated diameter of the spherical  $\text{Ag}_3\text{PO}_4$  particles was in the range of 200–300 nm. The TEM images (Fig. 2d and e) of the composite showed that the outer layer of the as-prepared  $\text{Ag}_3\text{PO}_4$ @PANI sample was distinctly different from the  $\text{Ag}_3\text{PO}_4$  core. This result was further confirmed by the high-resolution TEM images in Fig. 2f. These  $\text{Ag}_3\text{PO}_4$  particles were in intimate contact with the PANI, and the lattice fringes of  $\text{Ag}_3\text{PO}_4$  can be clearly identified in Fig. 2f. The lattice fringes of particles exhibited a spacing of 0.27 nm, which is in agreement with the spacing of the (210) plane of  $\text{Ag}_3\text{PO}_4$  and consistent with JCPDS card no. 06-0505 [32]. Compared with point contact structure of traditional composite materials, the core@shell three-dimensional structure of  $\text{Ag}_3\text{PO}_4$ @PANI has a larger contact area, which can significantly promote photo-induced charge separation. The overall process for the fabrication of the core@shell structure of  $\text{Ag}_3\text{PO}_4$ @PANI is shown in Fig. 2g. First, synthetic  $\text{Ag}_3\text{PO}_4$  particles were prepared by the precipitation method. The as-prepared particles were added to PANI (THF) solution and stirred at room temperature. Subsequently, the core@shell structure of PANI and  $\text{Ag}_3\text{PO}_4$  was formed by incubation of the PANI with  $\text{Ag}_3\text{PO}_4$  particles for 24 h, which minimized the surface energy of  $\text{Ag}_3\text{PO}_4$ @PANI.

The optical properties of the as-prepared samples were investigated by UV–vis diffuse reflectance spectra, as shown in Fig. 3. The light absorption edge of pure  $\text{Ag}_3\text{PO}_4$  was 520 nm, corresponding to a band gap ( $E_g$ ) of 2.45 eV [33]. After combination with PANI, a slightly red shift of the band edge, as well as an enhanced visible light response, was observed. The  $\text{Ag}_3\text{PO}_4$ @PANI composite showed significantly stronger light absorption than  $\text{Ag}_3\text{PO}_4$ . The band gap energy of a semiconductor could be calculated by the Kubelka-Munk equation [34]. As shown in Fig. 3b, the transition bandgaps estimated from the onset of the curve edges were about 2.45, 2.38, 2.21, 2.29, 2.24, and 2.13 eV for  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ag}_3\text{PO}_4$ @PANI (1 wt.%),  $\text{Ag}_3\text{PO}_4$ @PANI (5 wt.%),  $\text{Ag}_3\text{PO}_4$ @PANI (10 wt.%),  $\text{Ag}_3\text{PO}_4$ @PANI (15 wt.%), and  $\text{Ag}_3\text{PO}_4$ @PANI (20 wt.%), respectively. The relatively narrow band-gap energy observed for  $\text{Ag}_3\text{PO}_4$ @PANI is likely attributed to the strong interaction of the hybrid structure, which enables more efficient utilization of the solar spectrum. Furthermore, the formation of a conjugated structure between the  $\pi$ -conjugated structure of PANI and  $\text{Ag}_3\text{PO}_4$  over a wide range facilitates the migration efficiency of photo-induced charges and suppresses the charge recombination, thus enhancing the photocatalytic performance of  $\text{Ag}_3\text{PO}_4$ @PANI.

The Fourier transform infrared spectrometry (FTIR) spectra of PANI,  $\text{Ag}_3\text{PO}_4$ , and  $\text{Ag}_3\text{PO}_4$ @PANI composite photo-catalyst are shown in Fig. 4. The bands at  $1659\text{ cm}^{-1}$  and  $1381\text{ cm}^{-1}$  were attributed to the stretching and bending of H–O of water adsorbed on the surface, respectively [35–37]. The water molecules and hydroxyl groups adsorbed on the  $\text{Ag}_3\text{PO}_4$  surface can be converted to hydroxyl free radicals in the photocatalytic reaction for the oxidation of organic pollutants. The two peaks at  $1010\text{ cm}^{-1}$  and  $558\text{ cm}^{-1}$  in the FTIR spectrum of  $\text{Ag}_3\text{PO}_4$  were assigned to the P–O stretching vibration in  $\text{PO}_4^{3-}$ . The formation of  $\text{PO}_4^{3-}$  tetrahedral units with strong P–O bonds weakens the covalent nature of Ag–O bonds, inhibiting hybridization of Ag d with O p. This excludes the d character from the conduction-band minimum (CBM), leaving highly dispersive Ag s–Ag s hybrid bands





**Fig. 2.** SEM images of (a)  $\text{Ag}_3\text{PO}_4$ , (b)  $\text{Ag}_3\text{PO}_4$ @PANI, (c) TEM images of  $\text{Ag}_3\text{PO}_4$ , (d, e) TEM images of  $\text{Ag}_3\text{PO}_4$ @PANI, (f) HRTEM images of  $\text{Ag}_3\text{PO}_4$ @PANI, (g) The schematic illustration of the preparation of  $\text{Ag}_3\text{PO}_4$ @PANI composites.

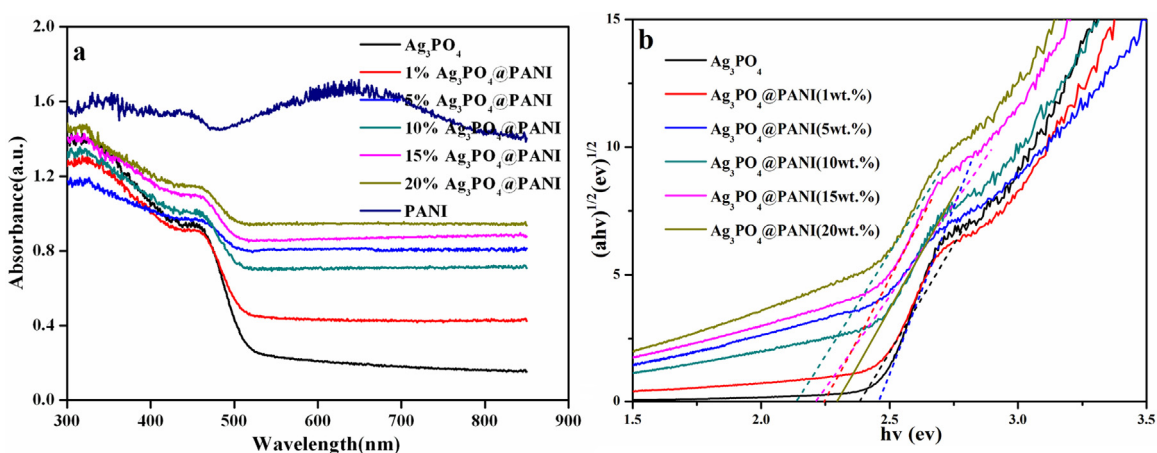


Fig. 3. (a) UV-vis diffuses reflectance spectra of the as-prepared  $\text{Ag}_3\text{PO}_4$ , PANI, and  $\text{Ag}_3\text{PO}_4$ @PANI. (b) Relationship of  $(ah\nu)^{1/2}$  vs.  $E$  (eV).

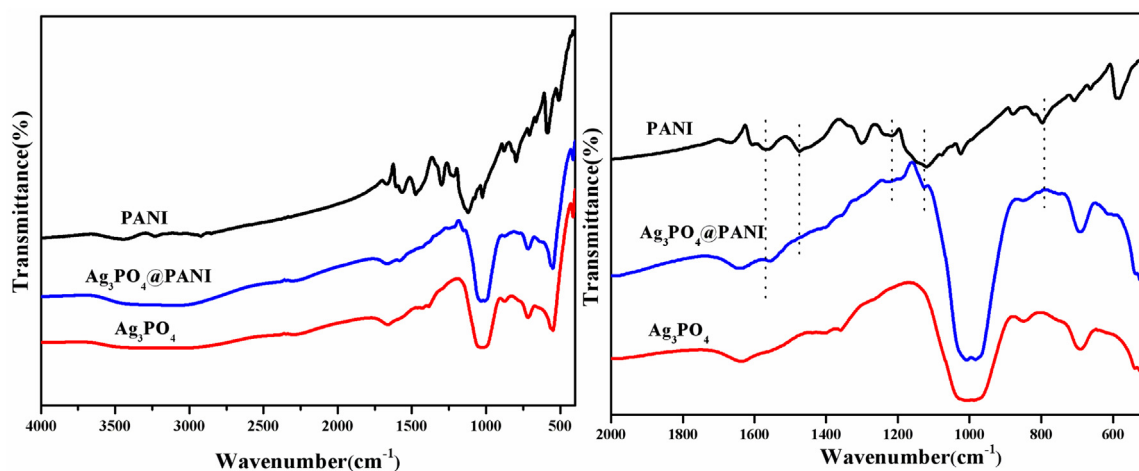


Fig. 4. FTIR spectra of  $\text{Ag}_3\text{PO}_4$ , PANI and  $\text{Ag}_3\text{PO}_4$ @PANI (5 wt.%).

[38]. The delocalized charge distribution of the CBM results in a small effective mass of the electron, which is favorable for the carrier transfer to the surface. The peaks of pure PANI at  $1560\text{ cm}^{-1}$  ( $\text{C}=\text{N}$  and  $\text{C}=\text{C}$  stretching modes) and  $1294\text{ cm}^{-1}$  ( $\text{C}-\text{N}$  stretching mode) shifted to lower wavenumbers [39], indicating that all of these chemical bonds were weakened. The red shift of these bands suggested that the bond strengths of  $\text{C}=\text{N}$  and  $\text{C}-\text{N}$  were reduced so that the PANI conjugated bond was stretched and a more conjugated structure containing PANI and  $\text{Ag}_3\text{PO}_4$  was formed. A similar chemical bonding was also observed in the case of  $\text{ZnO}$  [29] and  $\text{TiO}_2$  [40] hybrid monolayer polyaniline composite, as reported by Zhu et al. Compared with the point contact, the core@shell structure having a large contact area is more conducive to the formation of the interaction. This interaction is essential to promote the separation efficiency of photo-generated carriers and to enhance photocatalytic activity and anti-photocorrosion performance of  $\text{Ag}_3\text{PO}_4$ @PANI photocatalyst.

Raman spectroscopy analysis was further performed to confirm the interaction in the  $\text{Ag}_3\text{PO}_4$ @PANI composite. Fig. 5a shows the Raman spectra of  $\text{Ag}_3\text{PO}_4$ , PANI, and  $\text{Ag}_3\text{PO}_4$ @PANI composite. The strong absorption peak at  $912\text{ cm}^{-1}$  in the spectrum of  $\text{Ag}_3\text{PO}_4$  can be assigned to the vibration of terminal oxygen bond of phosphate group [41]. The distinct Raman peak at  $567\text{ cm}^{-1}$  corresponded to the symmetric stretch of  $\text{P}-\text{O}-\text{P}$  bonds. For the Raman spectrum of PANI, the bands around  $1596\text{ cm}^{-1}$  were attributed to the vibrational mode of the benzenoid unit. A peak near  $1476\text{ cm}^{-1}$  was

assigned to the vibrational mode of the quinonoid unit, and the peak at about  $1173\text{ cm}^{-1}$  was the characteristic vibrational mode of the  $\text{C}-\text{H}$  bending [39]. In the  $\text{Ag}_3\text{PO}_4$ @PANI composite, all of these bands shifted to lower wavenumbers. The red shift of these bands suggested that the bond strengths of  $\text{C}=\text{N}$  ( $\text{C}=\text{C}$ ) and  $\text{C}-\text{N}$  were weakened so that the PANI conjugated bond was stretched and a more conjugated structure containing PANI and  $\text{Ag}_3\text{PO}_4$  was formed. On the basis of these results, it can be concluded that an intense interaction existed between PANI and  $\text{Ag}_3\text{PO}_4$ . The TG curves of  $\text{Ag}_3\text{PO}_4$ , PANI, and  $\text{Ag}_3\text{PO}_4$ @PANI (5 wt.%) are shown in Fig. 5b. It is evident that the thermal degradation of pure PANI consisted of two distinct stages. The first stage occurring from 100 to  $300^\circ\text{C}$  was attributed to desorption of solvent, and the second stage extending from 350 to  $800^\circ\text{C}$  was mainly caused by the chemical desorption and decomposition of PANI. The TG curves of  $\text{Ag}_3\text{PO}_4$ @PANI (5 wt.%) underwent a two-step weight loss pattern. The stage extending from 200 to  $650^\circ\text{C}$  with a weight loss of 4.8% was attributed to the decomposition of PANI. The amount of weight loss was nearly equivalent to the amount of PANI (5.0%) coated on  $\text{Ag}_3\text{PO}_4$ . Moreover, the  $\text{Ag}_3\text{PO}_4$ @PANI (5 wt.%) sample hardly showed weight loss in the range of  $100\text{--}300^\circ\text{C}$ , indicating a strong chemical interaction took place between  $\text{Ag}_3\text{PO}_4$  and PANI. This strong chemical interaction limited the thermal motion of the polymer chain and increased the thermal degradation temperature, thereby enhancing the thermal stability of  $\text{Ag}_3\text{PO}_4$ @PANI composite [42].

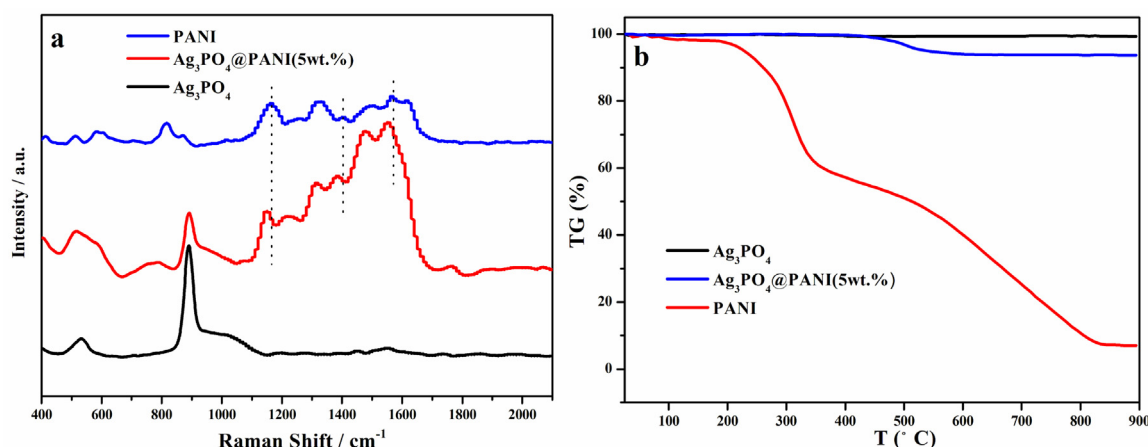
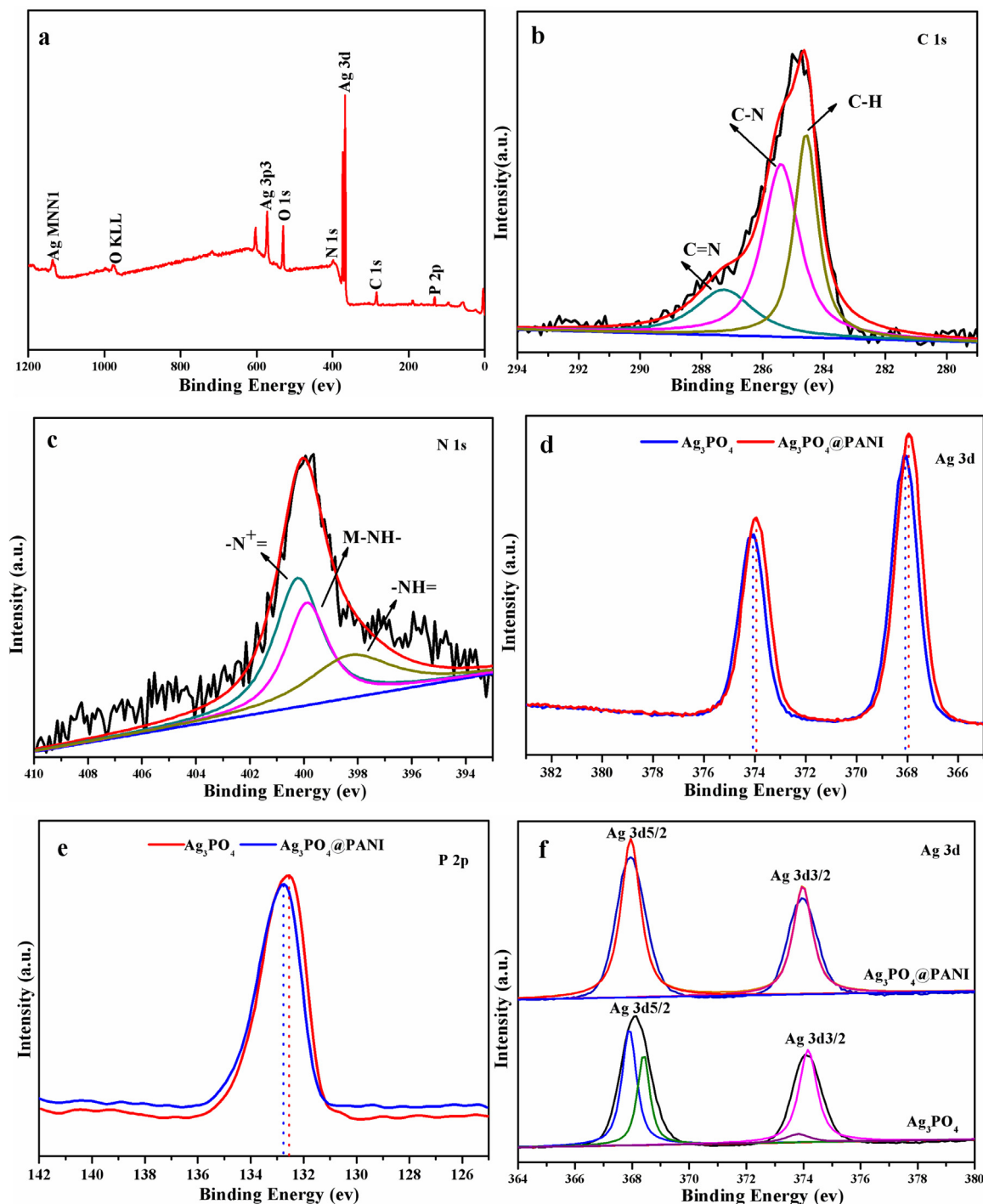


Fig. 5. (a) Raman spectra of Ag<sub>3</sub>PO<sub>4</sub>, PANI and Ag<sub>3</sub>PO<sub>4</sub>@PANI (5 wt.%), (b) TG curves of Ag<sub>3</sub>PO<sub>4</sub>, PANI and Ag<sub>3</sub>PO<sub>4</sub>@PANI (5 wt.%).

(XPS) analysis of Ag<sub>3</sub>PO<sub>4</sub> and Ag<sub>3</sub>PO<sub>4</sub>@PANI was carried out to reveal more detail information about the interaction between PANI and Ag<sub>3</sub>PO<sub>4</sub>. Fig. 6a presents the survey spectra of Ag<sub>3</sub>PO<sub>4</sub>@PANI. The binding energies of typical three peaks of C 1s of Ag<sub>3</sub>PO<sub>4</sub>@PANI were at 284.2, 285.3, and 287 eV (Fig. 6b), corresponding to C–H or C=C, C–N, and C=N, respectively. The N 1s spectrum of Ag<sub>3</sub>PO<sub>4</sub>@PANI represented quinonoid diimine at 398.9 eV, benzenoid imine at 399.7 eV, and protonation imine at 400.8 eV. Moreover, an additional peak at 398.8 eV was observed, due to the formation of a new metal–N bond (Fig. 6c) [43]. The presence of M–NH– indicated that there was a chemical interaction between the  $\pi$ -conjugated structure of Ag<sub>3</sub>PO<sub>4</sub> and PANI, which resulted in a larger conjugated system in Ag<sub>3</sub>PO<sub>4</sub>@PANI composite. Compared with Ag<sub>3</sub>PO<sub>4</sub>, both the binding energies of Ag and P shifted slightly in Ag<sub>3</sub>PO<sub>4</sub>@PANI (Fig. 6d and e), indicating there was an intense interfacial interaction between Ag<sub>3</sub>PO<sub>4</sub> and PANI [44]. The increased binding energy of surface atoms suggested that the Ag<sub>3</sub>PO<sub>4</sub>@PANI was more stable under visible-light irradiation than the pure Ag<sub>3</sub>PO<sub>4</sub>. Fig. 6f displays the Ag 3d level spectrum. For pure Ag<sub>3</sub>PO<sub>4</sub>, the Ag 3d<sub>3/2</sub> and Ag 3d<sub>5/2</sub> spin-orbital photoelectrons were located at binding energies of 373.99 eV and 367.94 eV, respectively. The Ag 3d<sub>3/2</sub> peak was further divided into two different peaks at 373.8 and 374.15 eV, and the Ag 3d<sub>5/2</sub> was also split into two distinct peaks at 367.89 and 368.4 eV. According to the report [45] by Zhang et al., the Ag 3d peaks with the binding energies of 373.8 and 367.89 eV corresponded to the Ag<sup>+</sup>. In addition, the peaks at 374.15 and 368.4 eV were attributed to metallic silver, and these two peaks with a spin energy separation of 6.1 eV further indicated that the Ag<sup>0</sup> existed in the Ag<sub>3</sub>PO<sub>4</sub> composite [46]. However, the peaks of Ag<sub>3</sub>PO<sub>4</sub>@PANI at 368.4 and 374.15 eV did not exhibit a split peak, indicating that the presence of Ag<sup>+</sup> in the sample. These observations further confirmed that the incorporation of PANI into Ag<sub>3</sub>PO<sub>4</sub> photocatalyst could substantially enhance the stability of Ag<sub>3</sub>PO<sub>4</sub>.

Transient photocurrent responses were determined to investigate the photoelectric responses of the photoelectrodes. As shown in Fig. 7a, the Ag<sub>3</sub>PO<sub>4</sub>@PANI (5 wt.%) produced a much higher photocurrent than both Ag<sub>3</sub>PO<sub>4</sub> and PANI under same conditions. This indicated that the combination of Ag<sub>3</sub>PO<sub>4</sub> and PANI was able to facilitate the photoinduced charge migration efficiently, which was a result of the hybridization effect in the Ag<sub>3</sub>PO<sub>4</sub>@PANI composite. From these results, it could be concluded that the highly enhanced photocurrent response of Ag<sub>3</sub>PO<sub>4</sub>@PANI is attributed to the superior charge mobility derived from the  $\pi$ -conjugation in the structure of PANI and to the formation of the new chemical bond between PANI and Ag<sub>3</sub>PO<sub>4</sub>. In general,

PL emission spectra are useful to reveal the efficiency of photo-generated carrier trapping, migration, transfer, separation, and recombination. Fig. 7b presents the PL emission spectra of Ag<sub>3</sub>PO<sub>4</sub> and Ag<sub>3</sub>PO<sub>4</sub>@PANI composite. The luminous peak of these photocatalysts was observed at around 525 nm. Compared with pure Ag<sub>3</sub>PO<sub>4</sub>, the intensity of the Ag<sub>3</sub>PO<sub>4</sub>@PANI composite displayed a considerable decrease in fluorescence. The quenched fluorescence indicated an efficient separation of photo-generated electron-hole pairs, which resulted in enhanced photocatalytic degradation performance of Ag<sub>3</sub>PO<sub>4</sub>@PANI composite. Photoelectrochemical measurements were carried out to study the photoelectrocatalytic performance. EIS has been proven to be a significant tool for the investigation of the charge transfer process on the electrode and at the interfacial contact between the electrode and electrolyte. This method is generally used to probe the separation efficiency of photo-induced charges. Fig. 7c shows a typical EIS of the prepared samples. The equivalent circuit (inset in Fig. 7c) of the device was conducted to analyze further the impedance spectra, which were fitted using the ZSimpWin software. R1 is the series resistance of the system. The first semi-circle (high frequency) can be assigned to the charge-transfer resistance (R2) of the Pt counter electrode/electrolyte interface. The second semi-circle (middle frequency) can be assigned to the charge-transfer resistance (R2) of the as-prepared sample anode/electrolyte interface. The R3 represents the charge transfer resistance in Helmholtz layer, whereas CPE represents the chemical capacitance. Fig. 7c shows the semi-circular Nyquist plot. It clearly indicated that the diameter of the arc radius on the EIS Nyquist plot of the Ag<sub>3</sub>PO<sub>4</sub>@PANI (5 wt.%) composite electrode was much smaller than those of the Ag<sub>3</sub>PO<sub>4</sub> and PANI electrodes under visible light irradiation, implying that the Ag<sub>3</sub>PO<sub>4</sub>@PANI photo-electrode exhibited the fastest interfacial charge transfer and the most efficient separation of photo-generated charge carriers compared with pure Ag<sub>3</sub>PO<sub>4</sub> and PANI. Fig. 7d showed that the characteristic peak of the Ag<sub>3</sub>PO<sub>4</sub>@PANI photo-electrode shifted from 387.38 Hz to 31.19 Hz, compared with that of pure Ag<sub>3</sub>PO<sub>4</sub>. The shift of a peak from a high frequency to a low frequency indicated a more rapid electron transfer process because frequency ( $f$ ) is closely related to the lifetime ( $\tau$ ) of the injected electrons according to the equation:  $\tau \approx 1/(2\pi f)$ . According to this equation, the electron lifetime of Ag<sub>3</sub>PO<sub>4</sub>@PANI (5.105 ms) was estimated to be 8.6 times higher than that of pure Ag<sub>3</sub>PO<sub>4</sub> (0.411 ms), which indicated a higher injected electron lifetime and considerably inhibited charge recombination in the Ag<sub>3</sub>PO<sub>4</sub> photo-electrode, resulting in enhanced charge separation efficiency and improved photoelectrocatalytic performance.

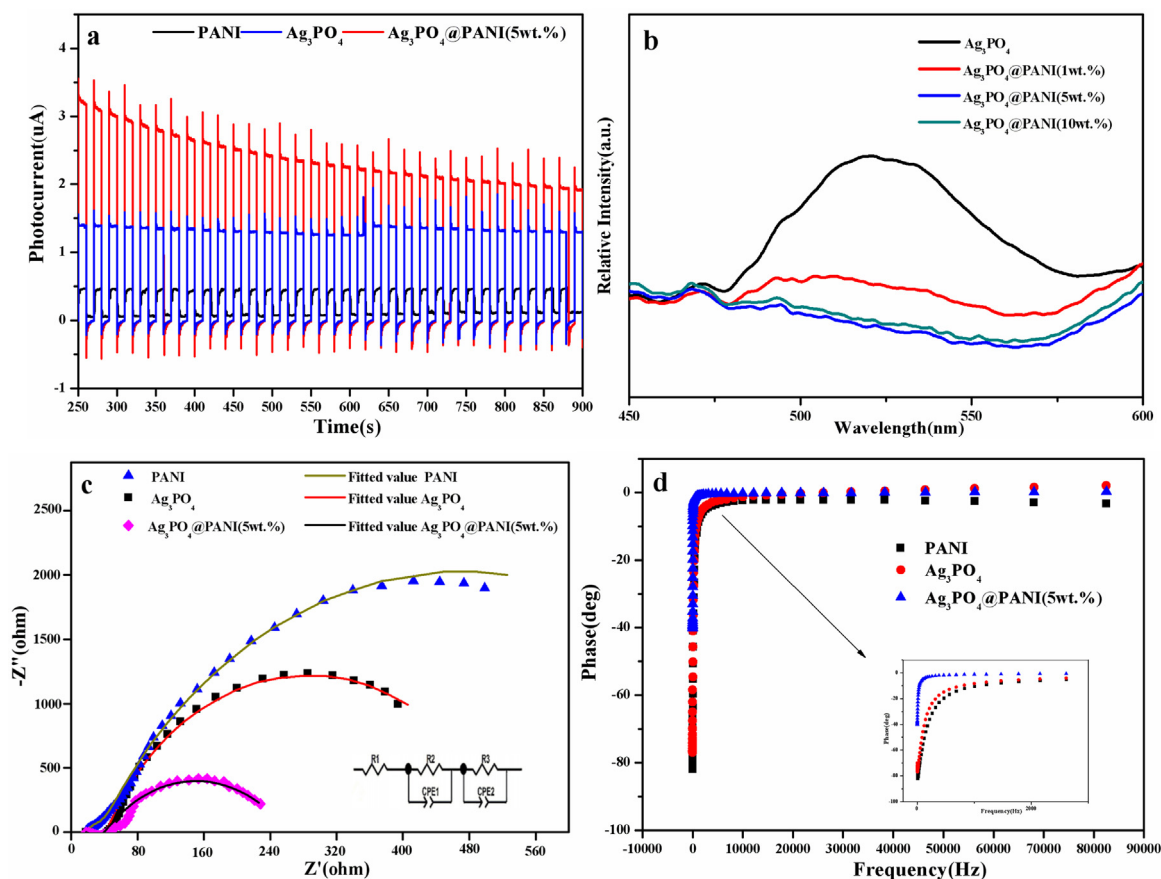


**Fig. 6.** The XPS spectra of  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4@\text{PANI}$ (5 wt.%): (a) survey spectra; (b) C 1s and (c) N 1s spectrum of  $\text{Ag}_3\text{PO}_4@\text{PANI}$ (5 wt.%); (d) Ag 3d; (e) P 2p; (f) Ag 3d of  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4@\text{PANI}$ (5 wt.%), respectively.

The photocatalytic activities of different samples for the phenol degradation under the visible light are shown in Fig. 8. As shown in Fig. 8a, phenol was only slightly degraded in the absence of the catalyst or the presence of the catalyst in the dark, indicating that the blank photolytic degradation was negligible. In contrast, nearly 100% of phenol was degraded with 30 min irradiation in the presence of  $\text{Ag}_3\text{PO}_4@\text{PANI}$  photocatalyst, which demonstrated the excellent photocatalytic activity of  $\text{Ag}_3\text{PO}_4@\text{PANI}$ . The photocatalyst prepared by simple mechanical mixing  $\text{Ag}_3\text{PO}_4$  with PANI (5 wt.%) in an agate mortar only degraded 83% of phenol under the same conditions. Similarly, Only 69% phenol was degraded by pure

$\text{Ag}_3\text{PO}_4$  under visible light irradiation for 30 min. The phenol degradation in the presence of PANI was also investigated under the same conditions. It turned out that phenol was slightly degraded in the presence of PANI only. These results indicated that  $\text{Ag}_3\text{PO}_4@\text{PANI}$  core@shell composite is a more efficient photocatalyst than pure  $\text{Ag}_3\text{PO}_4$ , PANI, and M- $\text{Ag}_3\text{PO}_4/\text{PANI}$  (5 wt.%). Fig. 8b shows the HPLC chromatogram during the photo-degradation of phenol over  $\text{Ag}_3\text{PO}_4@\text{PANI}$  (5 wt.%) under visible light irradiation. The phenol showed a characteristic peak with a retention time (RT) of 4.7 min [47]. The phenol peak became weaker with increasing irradiation time and disappeared completely after 30 min, indicating the excel-





**Fig. 7.** (a) Transient photocurrent responses of pure  $\text{Ag}_3\text{PO}_4$ , PANI, and  $\text{Ag}_3\text{PO}_4@\text{PANI}$ , (b) The photoluminescence spectra of the prepared  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ag}_3\text{PO}_4@\text{PANI}$ , (c) EIS plots of the samples under irradiation with visible light. Inset: equivalent circuit used to fit the data. (d) the Bode-phase of pure  $\text{Ag}_3\text{PO}_4$ , PANI, and  $\text{Ag}_3\text{PO}_4@\text{PANI}$ .

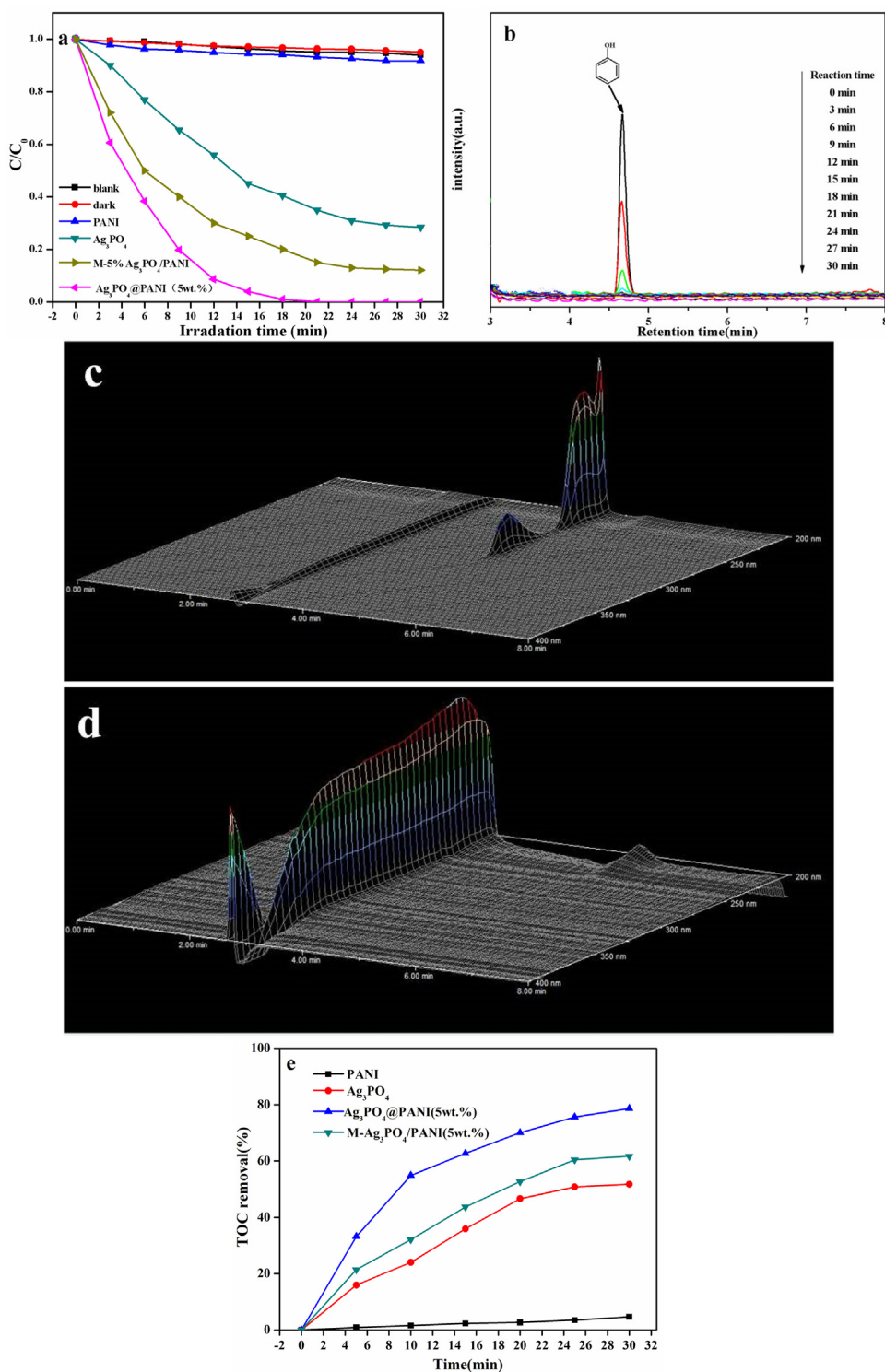
lent photocatalytic activity of  $\text{Ag}_3\text{PO}_4@\text{PANI}$ . Three-dimensional HPLC chromatographic analysis was conducted to further evaluate the photocatalytic activity of the  $\text{Ag}_3\text{PO}_4@\text{PANI}$  (5 wt.%). The retention time and shape of peak reflected the degradation of phenol in solution. As shown in Fig. 8c, in the reaction time of 0 min, HPLC solvent peak and phenol corresponding peak were observed in the chromatogram. After 30 min illumination, only the HPLC solvent peak was observed in the chromatogram, and the peaks corresponding to phenol disappeared (Fig. 8d), demonstrating that phenol was degraded to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the process of photocatalytic reaction. To further elucidate the degradation products and degradation pathway of phenol in the presence of  $\text{Ag}_3\text{PO}_4@\text{PANI}$ , we conducted photocatalytic experiments with prolonged irradiation times (30 min). It was found that the as-prepared  $\text{Ag}_3\text{PO}_4@\text{PANI}$  hybrid hydrogels exhibited enhanced performance in TOC removal of phenol solution. Fig. 8f shows the TOC removal of phenol as a function of reaction time. After 30 min illumination, the TOC removal by PANI,  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ag}_3\text{PO}_4@\text{PANI}$  (5 wt.%), M-5%  $\text{Ag}_3\text{PO}_4/\text{PANI}$  were 4.67%, 51%, 78%, 61%, respectively. This further illustrated that the photocatalytic activity and mineralization ability of  $\text{Ag}_3\text{PO}_4@\text{PANI}$  are obviously superior to other investigated catalysts.

Next, we investigated the effect of PANI content on the photocatalytic activity of  $\text{Ag}_3\text{PO}_4@\text{PANI}$  composite. Fig. 9 shows degradation rate (a) and first-order rate constant (b) of  $\text{Ag}_3\text{PO}_4@\text{PANI}$  composite. The photocatalytic performance significantly improved after the introduction of PANI and increased with the increase of PANI content from 1.0 to 5.0 wt.%. For example, the  $\text{Ag}_3\text{PO}_4@\text{PANI}$  composite containing 5.0 wt.% PANI degraded 100% of phenol and exhibited a photodegraded rate constant of  $0.2181 \text{ min}^{-1}$ , rep-

resenting an optimal coating amount with a high photocatalytic activity. However, further increasing the PANI content to 20 wt.% in the composite led to a decrease in photocatalytic activity. It also could be seen from the graph of Fig. 9 that the coating amount of PANI significantly affected the photocatalytic activity of the as-prepared samples. When the PANI content was relatively low (<5.0 wt.%), the contact area gradually increased with the increment of PANI. Therefore, an effective charge separation can be achieved, resulting in enhancement of photocatalytic activity and inhibition of photo-corrosion. On the other hand, when the PANI content was relatively high (>5.0 wt.%), a significant amount of PANI formed a thick and completely closed shell on the  $\text{Ag}_3\text{PO}_4$  particles, which suppressed the transfer of electrons on the enriched  $\text{Ag}_3\text{PO}_4$  to the surface of PANI. Under the circumstance, it reduced the number of hydroxyl radical which can act as a dominant reactive species in the photocatalytic degradation. Simultaneously, this can facilitate the recombination of photoinduced electron-hole pairs. Consequently, the photocatalytic activity decreased rapidly with further increasing of the PANI content. These results demonstrated that the PANI shell could enhance the photocatalytic degradation activity, and proper thickness of PANI shell is critical for the enhancement of photocatalytic activity.

In the present work, the degradation of 2, 4-dichlorophenol over  $\text{Ag}_3\text{PO}_4@\text{PANI}$  under visible light irradiation (>420 nm) was also studied for the assessment of the photocatalytic performance of  $\text{Ag}_3\text{PO}_4@\text{PANI}$  composite. As can be seen from Fig. 10a, 2, 4-dichlorophenol was degraded with a degradation ratio of 68.6% over  $\text{Ag}_3\text{PO}_4$  under visible light irradiation for 30 min. The degradation ratio significantly increased to 95.3% over the  $\text{Ag}_3\text{PO}_4@\text{PANI}$  composite photocatalyst with a 30 min visible light irradiation.





**Fig. 8.** (a) The variation of phenol concentration over various photocatalysts under visible light irradiation (b) HPLC chromatograms of phenol solutions with  $Ag_3PO_4@PANI$  (5 wt.%) photocatalytic catalyst (c) Three-dimensional HPLC chromatographic spectra of phenol degradation (0 min) (d) Three-dimensional HPLC chromatographic spectra of phenol degradation (30 min) (e) TOC removal of phenol over various photocatalysts under visible light irradiation.

These results indicated that  $Ag_3PO_4@PANI$  could also be used for the removal of 2, 4-dichlorophenol via photocatalytic degradation rather than physical adsorption. Well-aligned band-structure and the strong interaction in the intimate contact interface enhance the charge separation, which results in excellent photocatalytic activity. To obtain more information about intermediate species formed during the degradation process, we analyzed the degradation mixture by HPLC analysis. As shown in Fig. 10b, the 2,

4-dichlorophenol showed a characteristic peak with a retention time (RT) of 6.1 min. By comparison of the retention time with the reference standards under the same operating conditions, benzoquinone (RT = 3.6 min) and 2-chlorohydroquinone (RT = 3.8 min) were identified to be the main degradation intermediates of 2, 4-dichlorophenol in  $Ag_3PO_4@PANI$  system [48,49]. As the reaction proceeded, the peak intensity of both 2, 4-dichlorophenol and intermediate species decreased with continuous irradiation. Neither 2,

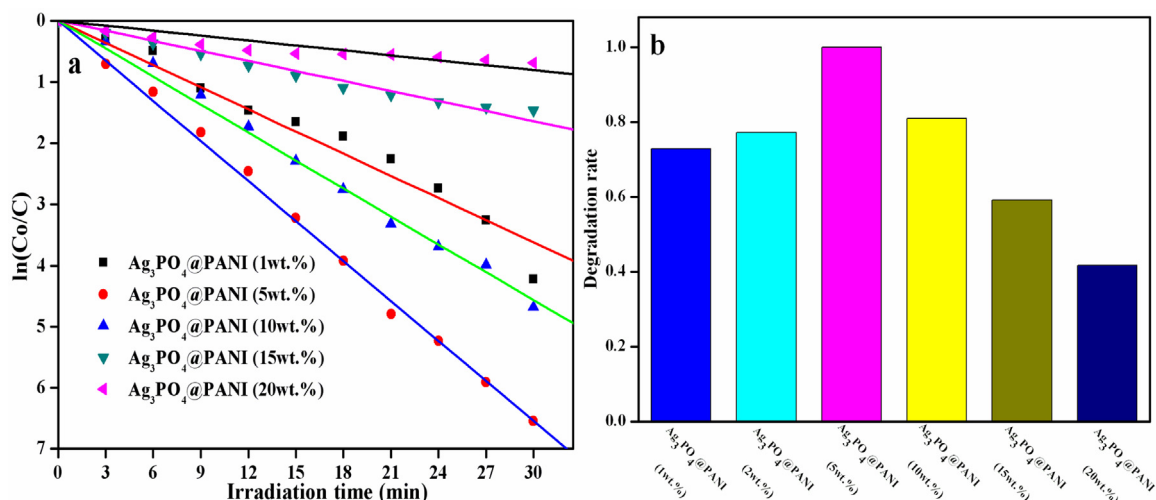


Fig. 9. Degradation rate (a) and first-order rate constant (b) of  $\text{Ag}_3\text{PO}_4$ @PANI composite with various PANI contents on degradation of phenol.

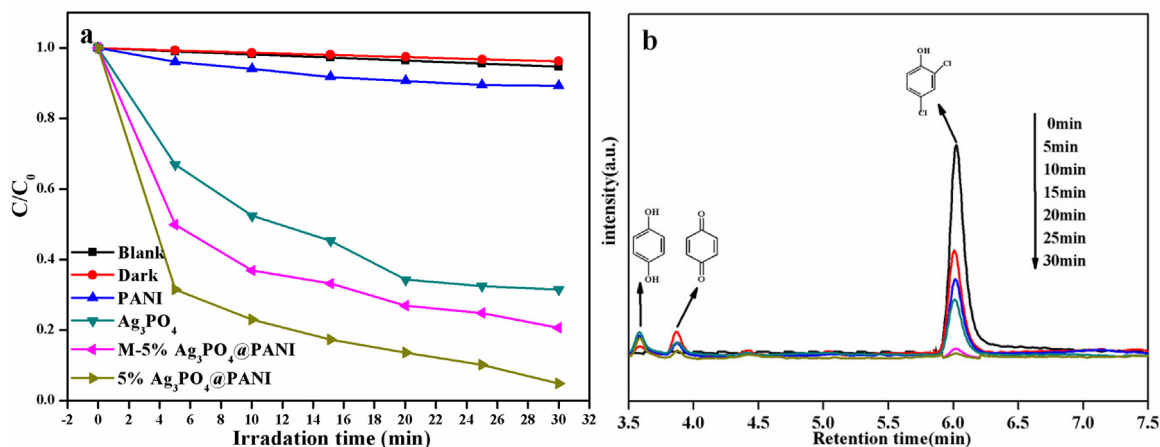


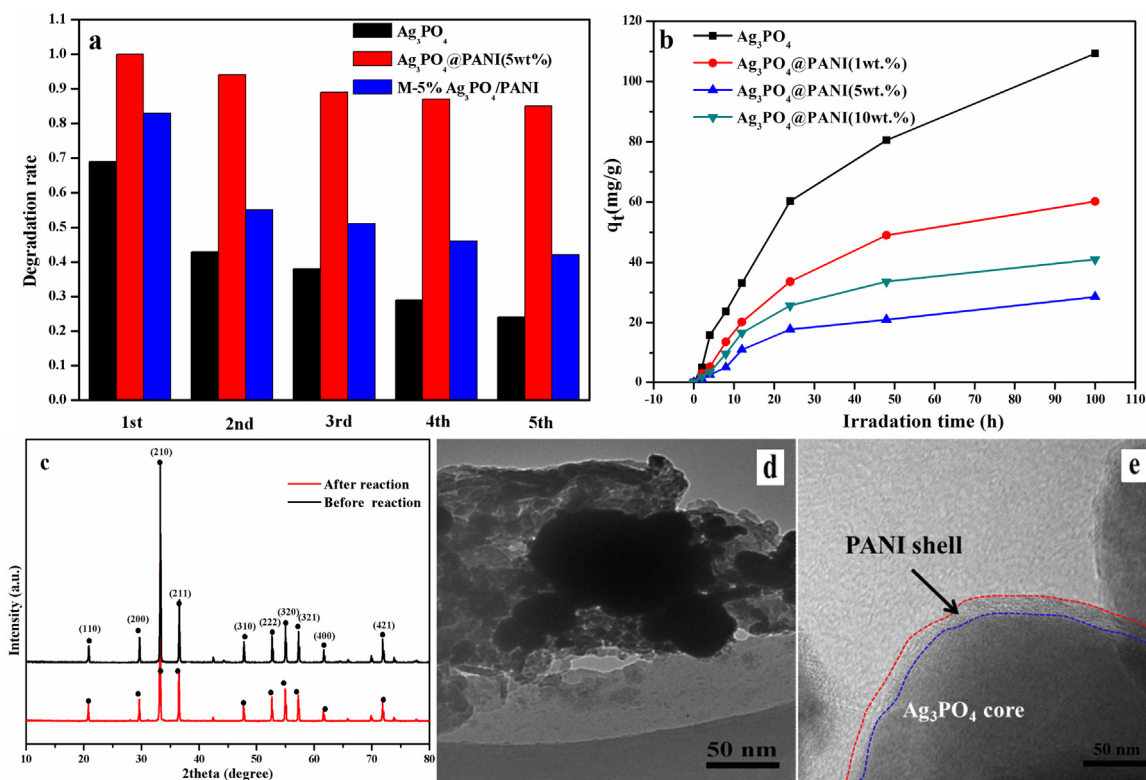
Fig. 10. (a) The variation of 2, 4-dichlorophenol concentration over various photocatalysts under visible light irradiation (b) Evolution of HPLC chromatograms for 2, 4-dichlorophenol solutions using  $\text{Ag}_3\text{PO}_4$ @PANI (5%) catalyst.

4-dichlorophenol nor intermediate species was detected after irradiated for 30 min, which indicated that 2, 4-dichlorophenol was mineralized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  completely.

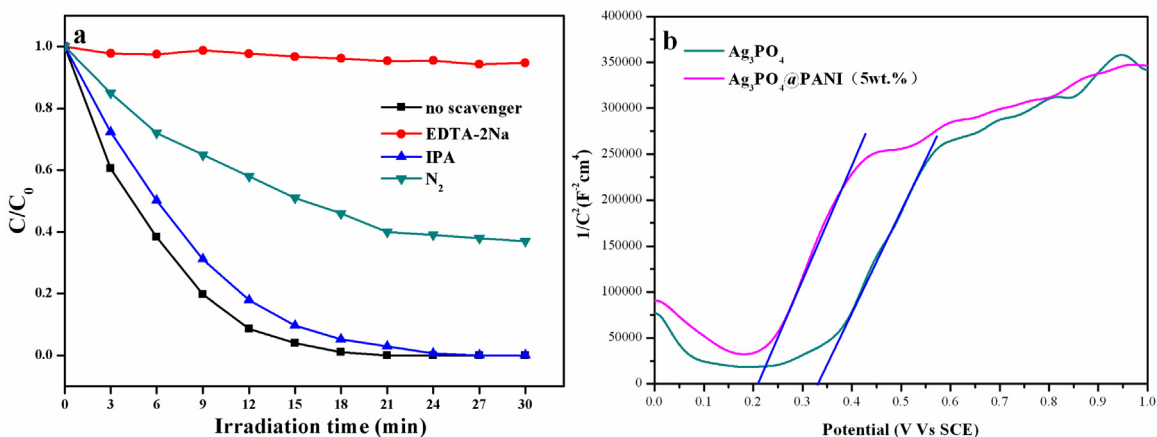
To test the stability of the  $\text{Ag}_3\text{PO}_4$ @PANI composite, we conducted a series of photostability experiments. Fig. 11a shows the photostability (phenol as a probe molecule) of  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ag}_3\text{PO}_4$ @PANI, M-5%  $\text{Ag}_3\text{PO}_4$ /PANI composite. As shown in Fig. 11a, the degradation over bare  $\text{Ag}_3\text{PO}_4$  decreased from 69% to 24% after five recycling runs. In contrast, 85% phenol was degraded over  $\text{Ag}_3\text{PO}_4$ @PANI composite after five recycling runs, indicating it has a high stability in the photocatalytic reaction under visible light irradiation. To investigate the stability of the catalyst in the aqueous solution, we determined the amounts of  $\text{Ag}^+$  from the dissolution of  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4$ @PANI in water under visible irradiation by using ICP.  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4$ @PANI (25 mg) were added to 100 mL of deionized water, and then 3 mL aliquots were sampled from the reactor at given intervals to analyze the concentrations of  $\text{Ag}^+$  in the aqueous solution. As can be seen from Fig. 11b, the dissolution of  $\text{Ag}_3\text{PO}_4$  in water proceeded rapidly during the reaction. When the visible light illumination time reached 100 h, the amount of  $\text{Ag}^+$  in water was determined to be about 109.30 mg/g. In contrast, due to the slow dissolution of  $\text{Ag}_3\text{PO}_4$ @PANI in water, the amount of  $\text{Ag}^+$  solution of  $\text{Ag}_3\text{PO}_4$ @PANI (1 wt.%),  $\text{Ag}_3\text{PO}_4$ @PANI (5 wt.%), and  $\text{Ag}_3\text{PO}_4$ @PANI (10 wt.%) were 60.23, 28.58, and 40.96 mg/g after 100 h, demonstrating that the proper PANI shell thickness coated on

the surface of  $\text{Ag}_3\text{PO}_4$  particles could effectively prevent it from dissolution in the aqueous solution. Therefore, the proper PANI shell can significantly increase the structural stability of  $\text{Ag}_3\text{PO}_4$ @PANI during the photocatalytic reaction. To assess the structural stability, we examined the crystalline structures of  $\text{Ag}_3\text{PO}_4$ @PANI composite before and after the experiment. As shown in Fig. 11c, no extra characteristic diffraction peaks were observed in XRD spectra pattern of  $\text{Ag}_3\text{PO}_4$ @PANI, which implied that there were no evident crystalline structure changes after the photocatalytic reaction. This result further confirmed that the PANI shell improved the stability of the  $\text{Ag}_3\text{PO}_4$  photocatalyst, which was also confirmed by TEM of the composite sample after the reaction. For pure  $\text{Ag}_3\text{PO}_4$  (Fig. 11d), after the photocatalytic cycles, the spherical particles disappeared, and web-like morphologies formed, indicating that the structure of the  $\text{Ag}_3\text{PO}_4$  crystal was demolished. As for  $\text{Ag}_3\text{PO}_4$ @PANI (Fig. 11e) after photocatalytic cycles under visible irradiation, it clearly showed that there was no formation of small Ag particles on the interface of  $\text{Ag}_3\text{PO}_4$  with PANI. Therefore, the incorporation of PANI into  $\text{Ag}_3\text{PO}_4$  photocatalyst not only enhanced the visible light photocatalytic performance of  $\text{Ag}_3\text{PO}_4$  but also inhibited the photo-corrosion, thereby resulting in enhanced stability of photocatalytic activity.

To elucidate the photocatalytic reaction mechanism, we attempted to investigate the main reactive species including  $\text{h}^+$ ,  $\text{O}_2^-$ , and  $\text{OH}^\bullet$  involved in the photocatalytic process [50–52]. In



**Fig. 11.** Recycling runs (a) of the degradation of phenol, (b) ICP of  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4/\text{PANI}$  composite in water (c) before and after the photocatalytic reaction. (d,e) TEM images of photocatalysts before and after photocatalytic degradation of phenol under visible light irradiation.



**Fig. 12.** (a) Plots of photogenerated active species trapped in the system of photodegradation of phenol by  $\text{Ag}_3\text{PO}_4/\text{PANI}$  under visible light (b) Mott-Schottky (MS) plots of pure  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4/\text{PANI}$ .

these experiments, EDTA-2Na,  $\text{N}_2$ , and isopropyl alcohol (IPA) were added to the photocatalytic reaction process as the scavengers for  $\text{h}^+$ ,  $\text{O}_2^-$ , and  $\text{OH}^\bullet$ , respectively. The detailed free radical capture experimental processes were similar to the photocatalytic experiments, and the results are shown in Fig. 12a. The results indicated that  $\text{OH}^\bullet$  was not the dominant active species in this process because the addition of isopropyl alcohol did not significantly inhibit the photocatalytic reaction. As depicted in Fig. 12a, the degradation rate decreased substantially to 5.36% in the presence of EDTA-2Na ( $\text{h}^+$  scavenger) while the degradation rate was 100% in the absence of scavengers, which suggested that  $\text{h}^+$  was the main reactive species for phenol degradation. Moreover, it could be seen that the photo-degradation process significantly decreased after  $\text{N}_2$  was introduced and that the photo-degradation rate was

considerably reduced by approximately 63%. The results indicated that superoxide radicals and direct holes were active species for the photocatalytic degradation. The effect of PANI on the band edge potential of  $\text{Ag}_3\text{PO}_4$  was investigated by Impedance Potential technique. As shown in Fig. 12b, the Mott-Schottky (MS) plots for  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4/\text{PANI}$  indicated they were typical n-type semiconductors with overall positive slopes. The flat-band potentials of  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4/\text{PANI}$ , calculated from the x-intercepts of the linear region, were found to be 0.33 V and 0.21 V vs. SCE. It is well-known that the potential of the conduction band in the n-type semiconductor is more negative by 0.1 V than that of the flat band potential [53]. Hence, the conduction band potentials (ECB) of  $\text{Ag}_3\text{PO}_4$  and  $\text{Ag}_3\text{PO}_4/\text{PANI}$  were determined to be 0.23 V and 0.11 V vs. SCE (equivalent to 0.47 V and 0.35 V vs. NHE), respec-

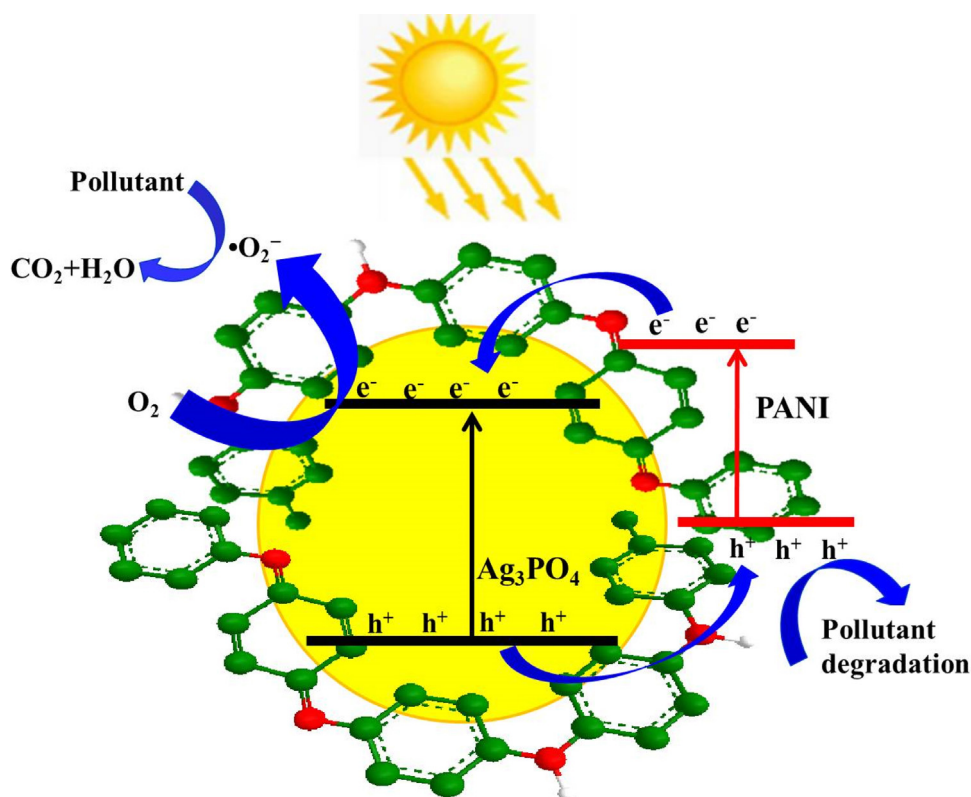


Fig. 13. Proposed photocatalytic mechanism for  $\text{Ag}_3\text{PO}_4/\text{PANI}$  composite under visible-light illumination.

tively. Apparently, the ECB of  $\text{Ag}_3\text{PO}_4/\text{PANI}$  composite showed a large negative shift of 0.12 V compared with that of pure  $\text{Ag}_3\text{PO}_4$ . It could be inferred that the electronic interactions between PANI and  $\text{Ag}_3\text{PO}_4$  caused a negative shift in the conduction band potential, which resulted in a highly positioned conduction band and a stronger reductive power for the  $\text{Ag}_3\text{PO}_4/\text{PANI}$  composite.

On the basis of the above analysis, a possible mechanism for the degradation of phenol of  $\text{Ag}_3\text{PO}_4/\text{PANI}$  composite under visible irradiation is proposed in Fig. 13. It is well known that both  $\text{Ag}_3\text{PO}_4$  and PANI can be excited to generate electrons and holes under visible light irradiation. Photo-generated electrons and holes are generated on the HOMO and LUMO of PANI when irradiated by visible light. The LUMO and HOMO potentials of PANI are  $-2.1$  and  $1.3$  eV, respectively, and CB and VB of  $\text{Ag}_3\text{PO}_4$  are  $0.47$  and  $2.92$  eV, respectively [54,55]. Since the LUMO potential of PANI is more negative than CB of  $\text{Ag}_3\text{PO}_4$ , the photo-generated electrons of PANI can be directly injected into the CB of  $\text{Ag}_3\text{PO}_4$  through the well-defined interface, and then react with oxygen molecules to generate  $\cdot\text{O}_2^-$  radicals [56]. Simultaneously, the excited holes produced by  $\text{Ag}_3\text{PO}_4$  are injected into the HOMO of PANI. Furthermore, since the specific  $\pi$ -conjugated structure PANI is an excellent material for transporting holes, the holes can be transferred easily to the surface and oxidize the adsorbed contaminants directly, which contributes to the dramatically visible activity of  $\text{Ag}_3\text{PO}_4/\text{PANI}$  photocatalyst in phenol degradation. As a result, the charge transfer efficiently inhibits the recombination of photo-generated electron-hole pairs, thereby enhancing the photocatalytic activity of  $\text{Ag}_3\text{PO}_4/\text{PANI}$  photocatalyst.

#### 4. Conclusion

In this work,  $\text{Ag}_3\text{PO}_4/\text{PANI}$  photocatalyst with core@shell structure was prepared by a chemisorption method. The results of this study indicated that the introduction of PANI significantly

improved the visible-light responsive photocatalytic activity of the  $\text{Ag}_3\text{PO}_4$  photocatalyst and the content of PANI dramatically affected the photocatalytic performance of  $\text{Ag}_3\text{PO}_4/\text{PANI}$  composite. The photocatalytic activities for degradation of phenol and 2, 4-dichlorophenol over  $\text{Ag}_3\text{PO}_4/\text{PANI}$  (5%) composite reached 100% and 95.3%, which were respectively 1.44 and 1.38 times of that of bulk  $\text{Ag}_3\text{PO}_4$ . The activity of  $\text{Ag}_3\text{PO}_4/\text{PANI}$  remained 85% after five cycling runs, whereas the activities of  $\text{M-Ag}_3\text{PO}_4/\text{PANI}$  (5 wt.%) and  $\text{Ag}_3\text{PO}_4$  only remained 42% and 24%, respectively, indicating that  $\text{Ag}_3\text{PO}_4/\text{PANI}$  photocatalyst possessed a superior stability. The enhancement of photocatalytic performance and stability is mainly attributed to the superior charge mobility derived from the  $\pi$ -conjugated structure of PANI and to the efficient separation and transfer of photo-generated electron-hole at the interface between PANI and  $\text{Ag}_3\text{PO}_4$  resulted from their matched energy level. In addition, PANI shell can prevent the dissolution of  $\text{Ag}_3\text{PO}_4$  particles in aqueous solution during the photocatalytic reaction, leading to a high stability of the  $\text{Ag}_3\text{PO}_4/\text{PANI}$  composite photocatalyst. In conclusion,  $\text{Ag}_3\text{PO}_4/\text{PANI}$  composite is a promising photocatalyst for the removal and degradation of organic pollutants in the environment.

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#### References

- [1] M.N. Chong, B. Jin, C.W.K. Chow, C. Saint, *Water. Res.* 44 (2010) 2997–3027.



- [2] R. Daghrir, P. Drogui, D. Robert, *Ind. Eng. Chem. Res.* 52 (2013) 3581–3599.
- [3] X.J. Wang, W.Y. Yang, F.T. Li, Y.B. Xue, R.H. Liu, Y.J. Hao, *Ind. Eng. Chem. Res.* 52 (2013) 17140–17150.
- [4] W.F. Shangguan, A. Yoshida, *J. Phys. Chem. B* 47 (2002) 12227–12230.
- [5] A. Kudo, K. Omori, H. Kato, *J. Am. Chem. Soc.* 49 (1999) 11459–11467.
- [6] J.W. Xu, Z.D. Gao, K. Han, Y.M. Liu, Y.Y. Song, *ACS Appl. Mater. Interfaces* 6 (2014) 15122–15131.
- [7] G. MaX, B. Lu, D. Li, *J. Phys. Chem. C* 11 (2011) 4680–4687.
- [8] Z.G. Yi, J.H. Ye, N. Kikugawa, *Nat. Mater.* 7 (2010) 559–564.
- [9] C.T. Dinh, T.D. Nguyen, F. Kleitz, T.O. Do, *Chem. Commun.* 47 (2011) 7797–7799.
- [10] C. Cui, Y.P. Wang, D.Y. Liang, W. Cui, H.H. Hu, B.Q. Lu, S. Xu, X.Y. Li, C. Wang, Y. Yang, *Appl. Catal. B: Environ.* 158 (2014) 150–160.
- [11] J.H. Liu, X. Li, F. Liu, L.H. Lu, L. Xu, L.W. Liu, W. Chen, L.M. Duan, Z.R. Liu, *Catal. Commun.* 46 (2014) 138–141.
- [12] Y.H. Yan, H.Y. Guan, S. Liu, R.Y. Jiang, *Ceram. Int.* 40 (2014) 9095–9100.
- [13] J. Yan, C. Wang, H. Xu, Y.G. Xu, X.J. She, J.J. Chen, Y.H. Song, H.M. Li, Q. Zhang, *Appl. Surf. Sci.* 287 (2013) 178–186.
- [14] C. Jin, G.L. Liu, L.H. Zu, Y. Qin, J.H. Yang, *J. Colloid Interface Sci.* 453 (2015) 36–41.
- [15] L. Liu, Y.H. Qi, J.S. Hu, Y.H. Liang, W.Q. Cui, *Appl. Surf. Sci.* 351 (2015) 1146–1154.
- [16] S. Khanchandani, S. Kundu, A. Patra, A.K. Ganguli, *J. Phys. Chem. C* 116 (2012) 23653–23662.
- [17] D.M. Chen, K.W. Wang, D.G. Xiang, R.L. Zong, W.Q. Yao, Y.F. Zhu, *Appl. Catal. B: Environ.* 147 (2014) 554–567.
- [18] L. Liu, J.C. Liu, D.D. Sun, *Catal. Sci. Technol.* 2 (2012) 2525–2532.
- [19] J.Q. Li, H. Yuan, Z.F. Zhu, *J. Colloid Interface Sci.* 462 (2016) 382–388.
- [20] Y. Wang, X. Li, Y. Wang, C. Fan, *J. Solid State Chem.* 202 (2013) 51–56.
- [21] G. Yu, J. Gao, J.C. Hummelen, F. Wudl, A.J. Heeger, *Science* 270 (1995) 1789–1791.
- [22] S. Zhu, T. Xu, H. Fu, J. Zhao, Y. Zhu, *Environ. Sci. Technol.* 41 (2007) 6234–6239.
- [23] G. Williams, B. Seger, P.V. Kamat, *ACS Nano* 2 (2008) 1487–1491.
- [24] X.C. Wang, S. Blechert, M. Antonietti, *ACS Catal.* 2 (2012) 1596–1606.
- [25] J. Wang, X.Y. Ni, *Solid State Commun.* 146 (2008) 239–344.
- [26] L. Liu, Y.H. Qi, J.L. Lu, S.L. Lin, W.J. An, Y.H. Liang, W.Q. Cui, *Appl. Catal. B: Environ.* 183 (2016) 133–141.
- [27] X. Li, G. Wang, X. Li, D. Lu, *Appl. Surf. Sci.* 229 (2004) 395–401.
- [28] M. Nandi, R. Gangopadhyay, A. Bhaumik, *Microporous Mesoporous Mater.* 109 (2008) 239–247.
- [29] H. Zhang, R.L. Zong, Y.F. Zhu, *J. Phys. Chem. C* 113 (2009) 4605–4611.
- [30] C. Wang, L. Wang, J. Jin, J. Liu, Y. Li, M. Wu, L.H. Chen, B.J. Wang, X.Y. Yang, B.L. Su, *Appl. Catal. B: Environ.* 188 (2016) 351–359.
- [31] Y.Y. Bu, Z.Y. Chen, *ACS Appl. Mater. Interfaces* 6 (2014) 17589–17598.
- [32] B.J. Jiang, Y.H. Wang, J.Q. Wang, C.G. Tian, W.J. Li, Q.M. Feng, Q.J. Pan, H.G. Fu, *ChemCatChem* 5 (2013) 1359–1367.
- [33] J.F. Ma, Q. Liu, L.F. Zhu, J. Zou, K. Wang, M.R. Yang, S. Komarneni, *Appl. Catal. B: Environ.* 182 (2016) 26–32.
- [34] C. Cui, Y.P. Wang, D.Y. Liang, W. Cui, H.H. Hu, B.Q. Lu, S. Xu, X.Y. Li, C. Wang, Y. Yang, *Appl. Catal. B: Environ.* 158–159 (2014) 150–160.
- [35] P.Y. Dong, Y.H. Wang, H.H. Li, H. Li, X.L. Ma, L.L. Han, *J. Mater. Chem. A* 1 (2013) 4651–4656.
- [36] Z.L. Xiu, H. Bo, Y.Z. Wu, X.P. Hao, *Appl. Surf. Sci.* 289 (2014) 394–399.
- [37] M. Thomas, S.K. Ghosh, K.C. George, *Mater. Lett.* 56 (2002) 386–392.
- [38] N. Umezawa, S.X. Ouyang, J.H. Ye, *J. Phys. Rev. B* 83 (2011) 1–8.
- [39] H. Zhang, Y.F. Zhu, *J. Phys. Chem. C* 114 (2010) 5822–5826.
- [40] H. Zhang, R.L. Zong, J.C. Zhao, Y.F. Zhu, *Environ. Sci. Technol.* 42 (2008) 3803–3807.
- [41] P.Y. Dong, Y.H. Wang, B.C. Cao, S.Y. Xin, L.N. Guo, J. Zhang, F.H. Li, *Appl. Catal. B: Environ.* 131–133 (2013) 45–53.
- [42] J.T. Feng, Y.H. Hou, X.Y. Wang, W.L. Quan, J.M. Zhang, Y.C. Wang, L.C. Li, *J. Alloys Compd.* 681 (2016) 157–166.
- [43] D.P. Wang, H.C. Zeng, *J. Phys. Chem. C* 113 (2009) 8097–8106.
- [44] M.T. Greiner, M.G. Helander, W.M. Tang, Z.B. Wang, J. Qiu, Z.H. Lu, *Nat. Mater.* 11 (2012) 79–81.
- [45] H. Zhang, G. Wang, D. Chen, X.J. Lv, J.H. Li, *Chem. Mater.* 20 (2008) 6543–6549.
- [46] Y.H. Liang, S.L. Lin, L. Liu, J.S. Hu, W.Q. Cui, *Appl. Catal. B: Environ.* 164 (2015) 192–203.
- [47] Y.Y. Bu, Z.Y. Chen, C.J. Sun, *Appl. Catal. B: Environ.* 179 (2015) 363–371.
- [48] X.J. Chen, Y.Z. Dai, X.Y. Wang, J. Guo, T.H. Liu, F.F. Li, *J. Hazard. Mater.* 292 (2015) 9–18.
- [49] W.J. Jiang, Y.F. Liu, J. Wang, M. Zhang, W.J. Luo, Y.F. Zhu, *Adv. Mater. Interfaces* (2015) 1500502.
- [50] M.C. Yin, Z.S. Li, J.H. Kou, Z.G. Zou, *Environ. Sci. Technol.* 43 (2009) 8361–8366.
- [51] Z.G. Zou, J.H. Ye, K. Sayama, H. Arakawa, *Lett. Nat.* 414 (2001) 625–627.
- [52] Y.L. Li, Y.M. Liu, J.S. Wang, E. Uchaker, Q.F. Zhang, S.B. Sun, Y.X. Huang, J.Y. Li, G.Z. Cao, *J. Mater. Chem. A* 1 (2013) 7949–7956.
- [53] A. Ishikawa, T. Takata, J.N. Kondo, M. Hara, H. Kobayashi, *J. Am. Chem. Soc.* 124 (2002) 13547–13553.
- [54] W.M. Wu, S.J. Liang, L.J. Shen, Z.X. Ding, H.R. Zheng, W.Y. Su, L. Wu, *J. Alloys Compd.* 520 (2012) 213–219.
- [55] X.F. Yang, H.Y. Cui, Y. Li, J.L. Qin, R.X. Zhang, H. Tang, *ACS Catal.* 3 (2013) 363–369.
- [56] J.F. Ma, Q. Liu, L.F. Zhu, J. Zou, K. Wang, M.R. Yang, S. Komarneni, *Appl. Catal. B: Environ.* 182 (2016) 26–32.